HUMIC ACIDS FROM SUBBITUMINOUS COAL -
A STUDY OF CONTROLLED DRY OXIDATION

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During the past few years, advances in humic acid chemistry have made it increasingly clear that humic acids offer an interesting and fairly direct route to large-scale chemical utilization of coal, and several commercial products containing (or derived from) them are, in fact, already being marketed (1,2,3). Despite this progress, however, processes by which humic acids form from and in coal are, like their detailed structure, still only incompletely understood and merit further investigation.

By definition, humic acids are brownish-black, alkali-soluble solids which can either be recovered from naturally weathered coals (4,5) or, alternatively, be prepared by controlled oxidation. The latter procedure, which is in principle to be preferred to reliance on necessarily random and somewhat uncertain natural processes, may take two basic forms. Pulverized coal can either be heated and re-acted with air or oxygen (or with an oxygen-enriched air stream), in fluidized or static bed (6,7,8,9,10); or the coal may be suspended, conventionally, in hot aqueous alkali and treated under pressure (11,12,13) with air or oxygen. The choice between these techniques appears, at this time, to be largely a matter of personal preference since each has distinct advantages and disadvantages. For example, while wet oxidation will generally entail a substantially shorter reaction period than the dry process, its greater severity will usually mean lower yields of humic acids (and a proportionately greater concentration of low molecular weight, water soluble, degradation products in the final product mixture)(11).

Regarding the formation of secondary degradation products as basically undesirable, the Research Council of Alberta concentrated an initial study of the mechanism of the coal ⟶ humic acid conversion on dry oxidation. This paper reports the behaviour of a typical Alberta subbituminous coal in such a process.

Experimental Procedure

In order to permit meaningful measurements which could be related to the ambient conditions under which oxidation was carried out, an apparatus of the form illustrated in Figures 1 and 2 was used. This afforded a gas-tight, closed circuit with provisions for pressure regulation, gas sampling and withdrawal of coal aliquots without interruption of the conversion process. As indicated in the diagrams, the total volume of the apparatus was approximately 2,200 cc.

Oxidation of the coal was achieved by means of dry oxygen which was introduced into the apparatus at the same rate at which it was consumed and which was thus maintained at a constant pre-selected pressure throughout each experiment. By arranging one-half of the constant-head oxygen supply bottle as a calibrated cylinder, accurate measurements of O_2-consumption rates were possible. The total pressure was maintained at 1 atmosphere.

Instantaneous oxygen concentrations within the apparatus were continuously recorded on a Beckman F3 oxygen analyzer.

At the commencement of a run, the oxygen bottle was filled and the measuring cylinder completely topped with water. 15.00 gm of coal (-65 + 150 mesh Tyler), vacuum dried at 50°C were then charged into the fluidizer, the CO_2 and H_2O absorbers weighed (to the nearest 0.01 gm) and the fluidizer brought to the selected reaction temperature.

During the first 30 minutes after attainment of the reaction temperature, the rate of oxygen consumption would occasionally exceed the capacity of the supply valve, and in such cases, oxygen was furnished from a secondary source. By this means, it was possible to maintain the oxygen content uniform within $\pm$ 1%.

As the run progressed, 1 cc gas samples were withdrawn from time to time and submitted to gas-chromatographic determination of oxygen (as a check on the performance of the Beckman analyzer), nitrogen (as a test for leaks) and carbon monoxide. At regular intervals, 0.1 - 0.2 gm coal samples were also withdrawn for infrared spectroscopy, elemental analysis and functional group determination.

Measurements of alkali-solubles in these coal samples — conventionally accepted as a measure of humic acid content — were made by Kreulen's method and expressed as percentage humic acids in the sample (14). A minor modification in Kreulen's method was however, introduced in order to secure greater precision. Since the results obtained are distinctly time-dependent (cf. Figure 3) — presumably because of further oxidation in aqueous alkali — and since this drift could not be eliminated by blanketing with N_2, humic acid contents were determined at 2 and 24 hours after initial suspension in alkali and extrapolated to zero time. Since the titre increased linearly with time for at least the first 30 hours after extraction, this procedure was considered justified and relatively error-free.

Results

Experiments so far have been limited to a single subbituminous coal with C $\sim$ 71%, H $\sim$ 4.2%. Results obtained are exemplified by Figure 4 which reproduces data gathered during a single experiment in which the oxygen concentration and temperature were held constant at 22.5% and 250°C, respectively. It will be observed that the carbon and hydrogen contents of the solid move asymptotically towards limiting values, while carboxylic acid concentration and total acidity (total acidity = carboxyl + phenolic OH) pass through a definite, broad maximum. The humic acid concentration likewise passes through a maximum. CO (not shown in Figure 4) appeared in the early stages of conversion, reached a maximum at 10 hours (5-15% by volume of gas) and disappeared completely beyond 65 hours. The significance of this observation is at this time unknown.

Material balances, which were established in all runs, checked within 5%. Experimental conditions could be duplicated to within ±1% in oxygen concentration and ±2°C in temperature, and the various measured quantities as shown in Figure 4 agreed to within ±5%.

Figure 5 represents a repeat of the experiment illustrated in Figure 4, but this time extended to 450 hours. No measurements were made before 150 hours had lapsed. Beyond the first 150 hours, only insignificant changes appear to take place in the composition of the solid, but as shown by the continuous oxygen consumption, there is a steady loss of coal and already formed humic acid to carbon dioxide and water. At the conclusion of the test, only 46% of the original charge was recovered as compared with 66% in the test stopped at 150 hours.

Similar experiments were carried out at temperatures between 150 and 300°C, and at oxygen concentrations between 10 and 100%. Figure 6 illustrates the relation between temperature and functional groups at constant oxygen concentration. The same relationship was found in tests where the oxygen concentration was varied.

A summary of 20 experiments so far concluded in the study here under review is contained in Figure 7a and b. For the particular coal examined in these runs, the pattern shows optimum humic acid conversion and recovery after 65 hours at 250°C and 25% oxygen concentration.

The humic acid content in the oxidized coal ran to ca. 95% and some 75% total solids (based on the initial charge) were recovered. The total (phenolic -OH plus -COOH) functional group concentration in the humic acid formed under these conditions runs to 10 milliequivalents/gm. The limiting C-H values are 61% and 1.8% respectively.

Discussion

Whether another coal would significantly alter the general pattern of results shown in Figure 7a and b, or whether it would only change the position of the maxima remains to be determined. Nor can anything, at this time, be said about possible catalytic effects of coal ash on the conversion process. Despite these limitations, however, the data so far at hand provide worthwhile new information.

As might be expected, variations in oxygen concentration and temperature tended to work in the same direction. Below 10% oxygen or 150°C, no significant reaction was observed. Above 80% oxygen or 300°C, rapid and complete oxidation of the coal to CO_2 and H_2O was found. For any conditions within this general range the carboxylic acid content rose through a maximum and then decreased (although the measurements were not always continued into the fall-off region). The total acidity likewise passed through a broad, but less pronounced maximum. These maxima occurred at shorter times as oxygen concentrations or temperatures increased.

The results illustrated in Figure 6 show that a temperature variation markedly influences the carboxyl concentration, which may range from 1 - 9 m.eq./gm. On the other hand, the total acidity is much less temperature dependent. Production of a humic acid principally characterized by either -OH or -COOH contents is, accordingly, dependent upon a more careful choice of experimental conditions than would be required if a predetermined total acidity only is to be afforded.

Since other results — though as yet incomplete — indicate that oxygen concentration has the same effect as temperature on the content and composition of the functional groups, the same statement may apply to this variable.

Another finding relates to the infrared spectra of partially reacted coal samples. These spectra, which were measured in order to gain information about reaction products not encompassed by other methods employed, did in some (but not all) series show pronounced absorption bands at 1850 and 1785 cm^{-1} and thereby indicate the existence of 5-membered ring cyclic anhydrides (15, 16). To our knowledge, such components have not previously been reported from studies of the coal ⟶ humic acid conversion and now raise the question of whether they are intermediates in the reaction sequence leading to humic acids or merely the result of dehydration of already formed humic acids. Because the answer to this question would provide experimental evidence for or against Tronov's postulates (17), suggesting that such cyclic anhydrides might be essential steps in the mechanism of conversion, a study pertaining to this problem is currently in progress in these laboratories.

Finally, some significance may be attached to the variations of carbon and hydrogen contents (cf. Figure 7a). The approach of these quantities to limiting values which cannot, apparently, be lowered by extending the reaction period, lends interesting experimental support to Francis' work on "oxidation tracks" and tends to validate the "limiting oxidation line" of his diagram (18). Prolonged oxidation, increased reaction temperatures, and/or higher oxygen concentrations appear to accomplish little more than conversion of carbon and hydrogen to CO_2 and H_2O respectively.

In the light of Figure 7a and b, it is obvious that optimum conditions for oxidation of a given coal, and for the production of a humic acid possessing predetermined properties, can be chosen with some ease. It is, however, equally obvious that artificial production of humic acids is subject to several limitations which arise as much from the meta-stability of humic acids as from the relatively low reaction rates. If it is accepted that humic acids hold an industrially important potential, further studies of their formation from coal are therefore imperative.
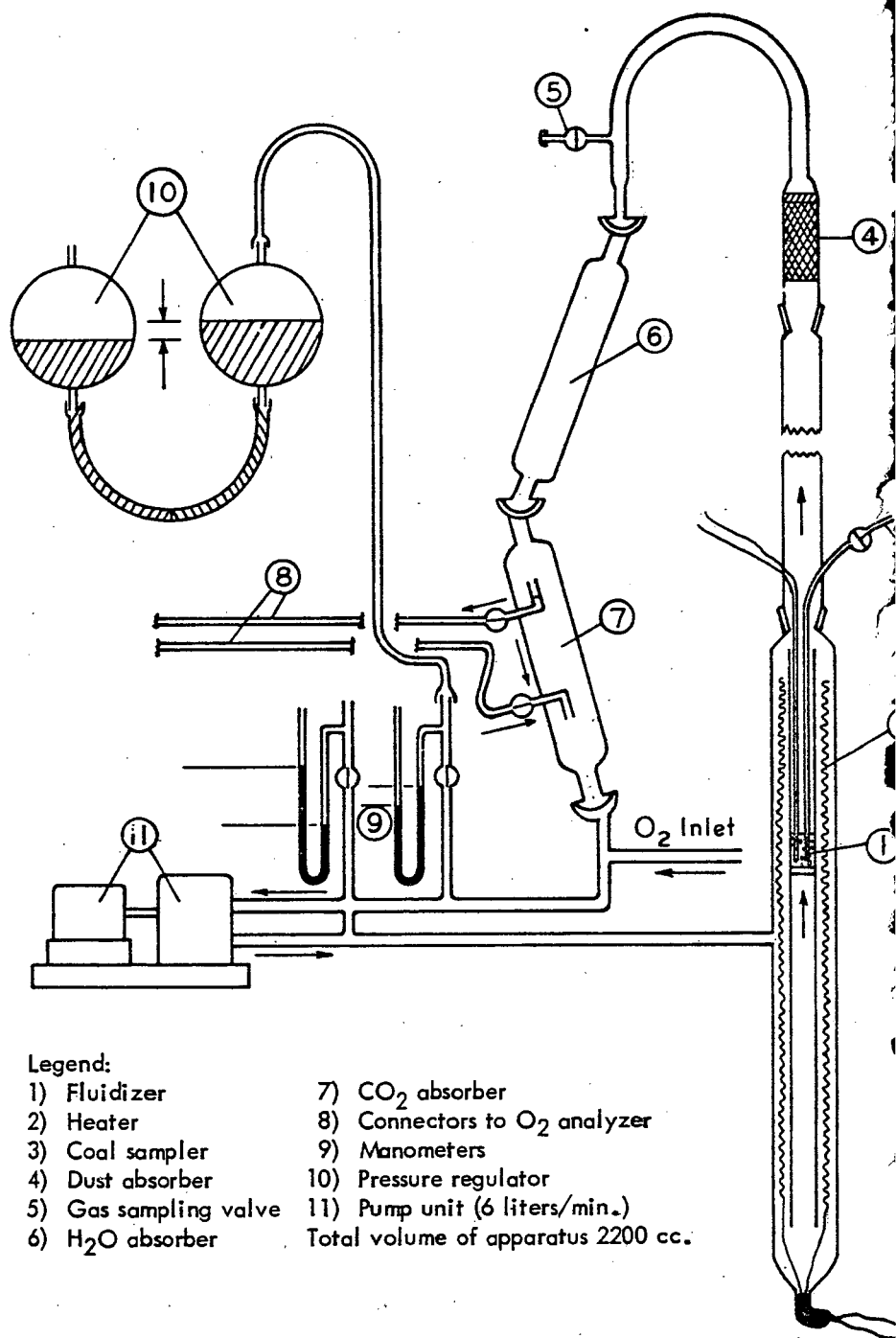
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FIGURE I

Legend:
1) Fluidizer
2) Heater
3) Coal sampler
4) Dust absorber
5) Gas sampling valve
6) H_2O absorber

7) CO_2 absorber
8) Connectors to O_2 analyzer
9) Manometers
10) Pressure regulator
11) Pump unit (6 liters/min.)
Total volume of apparatus 2200 cc.
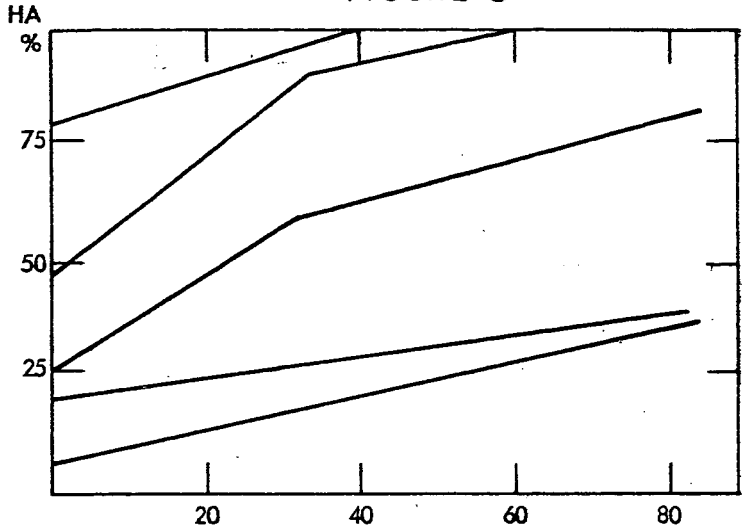
COAL OXIDATION APPARATUS
(not to scale)

FIGURE 2

Legend:
1) 4 liter O_2 – reservoir
2) 280 cm measuring column
3) Adjustable mercury-filter disc air trap for (2)
4) O_2 – trap
5) Manometer
6) H_2O absorber
7) Mercury bead capillary valve
8) Auxilliary valves

O_2

CaCl₂
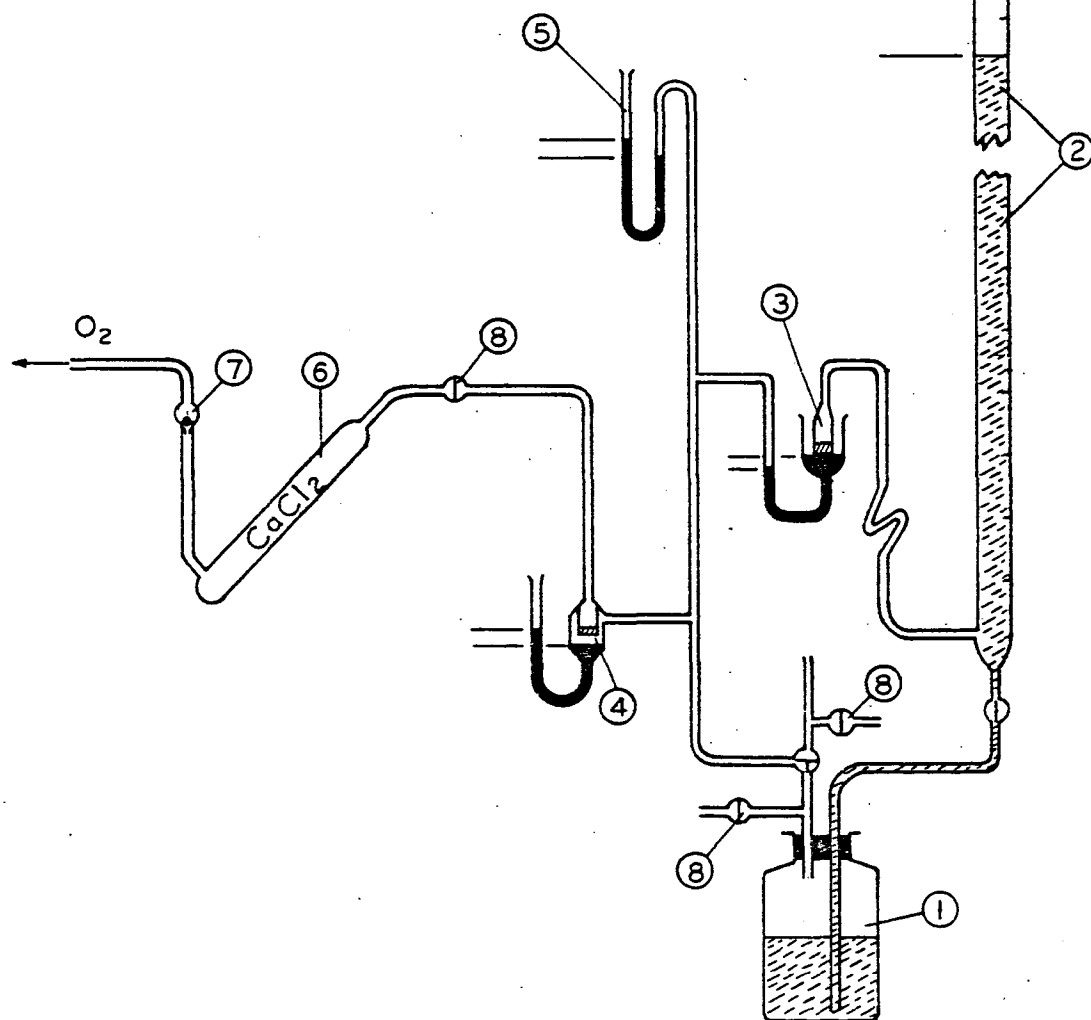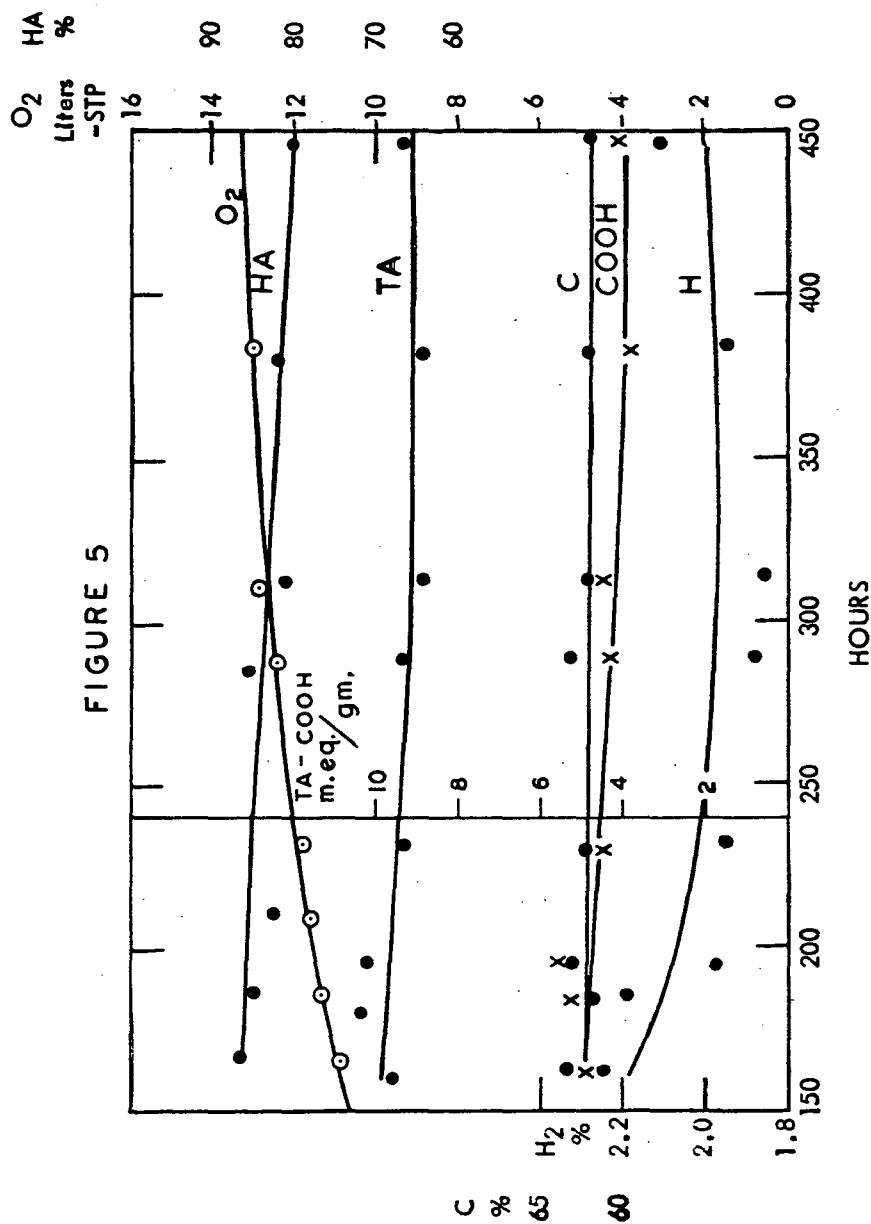
OXYGEN SUPPLY APPARATUS
(not to scale)

FIGURE 3

HOURS AFTER SUSPENSION IN ALKALI

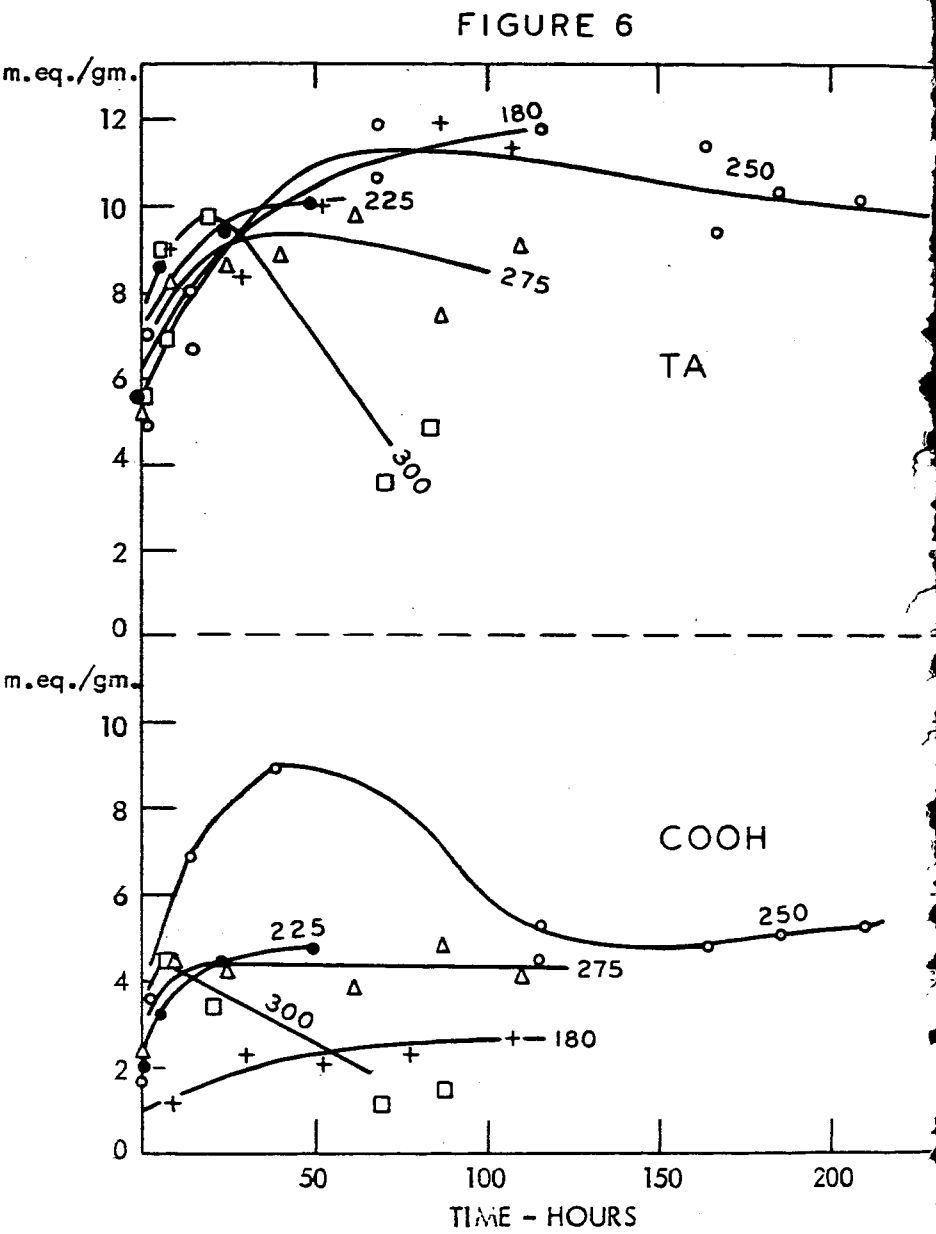Titration of humic acid content. Changes of titre with time

FIGURE 4

HOURS
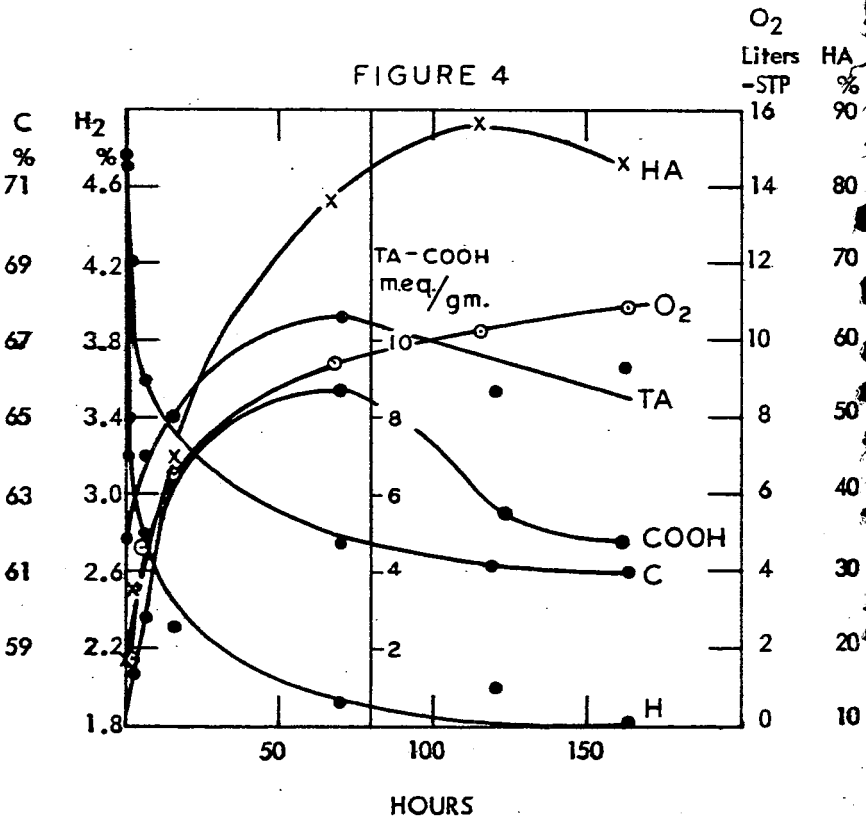
Variations of humic acid content and properties with time
Legend: HA = humic acid content in % of sample, TA = total acidity,
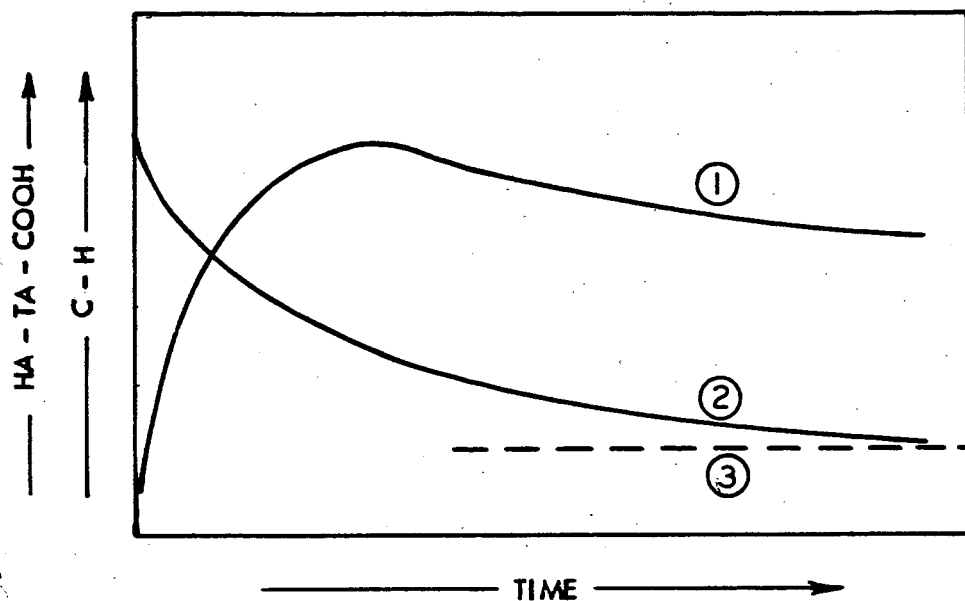COOH = carboxyl, C = carbon, H = hydrogen, O_2 = oxygen consumption

FIGURE 5

Variations in humic acid content and properties with time. Legend as in Figure 4

FIGURE 6

Variations in functional group content with temperature
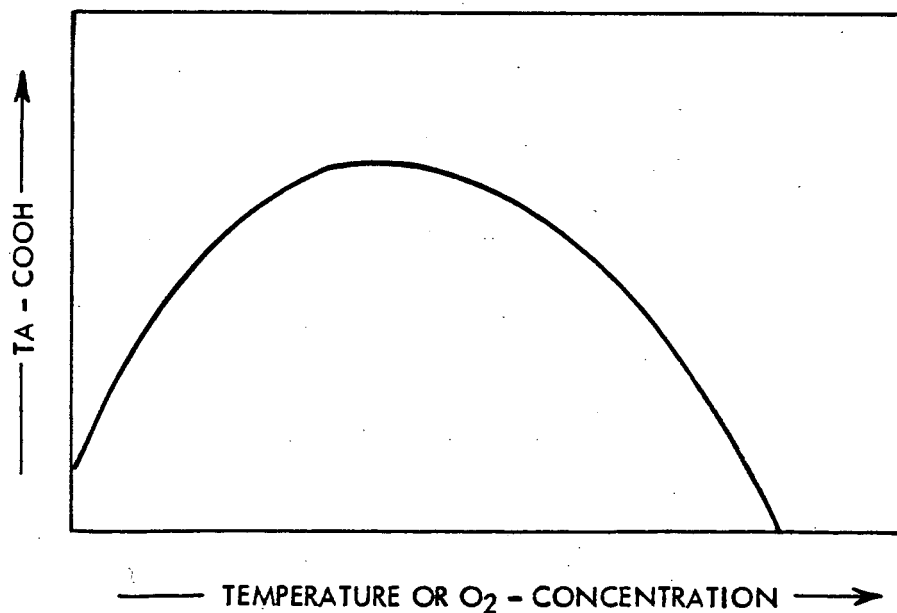
FIGURE 7 a

Variations of humic acid content and properties with time.
1) HA – COOH – TA 2) C – H 3) C – H limits

FIGURE 7 b

Variations in functional groups with temperature or O_2 – concentration